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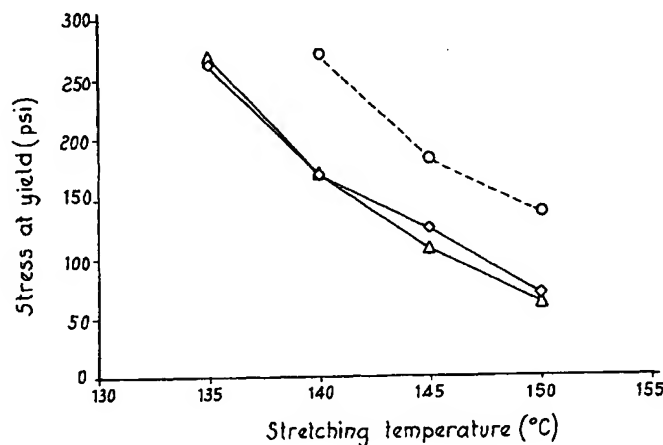
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(54) Title: BIORIENTED POLYPROPYLENE FILMS



○ = Comp. 1

△ = Ex. 1

◇ = Ex. 2

(57) Abstract: Bioriented polypropylene films (BOPP) wherein at least one layer comprises a propylene polymer containing at least 0.8% by weight of ethylene and optionally one or more C₄-C₁₀α-olefins, or a propylene polymer composition containing at least 0.8% by weight of one or more comonomers selected from ethylene and more C₄-C₁₀α-olefins, and having the following features: 1) a melting temperature of 155°C or higher; 2) a content of fraction soluble in xylene at room temperature lower than 3% by weight and a value of the ratio of the polymer fraction collected at the temperature range from 25°C to 95°C (by TREF) to the said xylene soluble fraction higher than 8.

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"BIORIENTED POLYPROPYLENE FILMS"

The present invention relates to improved bioriented polypropylene films (BOPP) based on a particular kind of propylene polymer or polymer composition.

Compared to BOPPs made of propylene homopolymers and copolymers with similar MFR, the films of the invention provide a better balance of elevated temperature draw characteristics and physical properties. Thus, at the same or even lower stretching temperature, the oriented films of the invention exhibit improved properties such as stiffness and oxygen barrier.

Moreover, when copolymer compositions are used for BOPPs according to the existing art, they are typically used for the layers to be heat-sealed (surface layers), and good properties (in particular heat-sealing properties) are generally obtained at elevated contents of the fraction soluble in hydrocarbon solvents, as shown for example in US A 5,780,168. However, elevated solvent-soluble contents make the film unsuitable for use in food packaging.

It has now been found that by properly selecting some intrinsic properties of the propylene polymer material, BOPPs with excellent properties and low solvent-soluble contents are obtained.

Therefore the present invention provides bioriented polypropylene films (BOPP) wherein at least one layer comprises a propylene polymer containing at least 0.8% by weight of ethylene and optionally one or more C₄-C₁₀ α -olefins, or a propylene polymer composition containing at least 0.8% by weight of one or more comonomers selected from ethylene and C₄-C₁₀ α -olefins, and having the following features:

- 1) a melting temperature of 155 °C or higher;
- 2) a content of fraction soluble in xylene at room temperature (about 25 °C) lower than 3% by weight, preferably lower than 2.5% by weight, and a value of the ratio of the polymer fraction collected at the temperature range from 25°C to 95°C (by TREF: temperature rising elution fractionation with xylene) to the said xylene soluble fraction, higher than 8 wt%/wt%, preferably higher than 10, wt%/wt%, more preferably higher than 12 wt%/wt%.

In a preferred embodiment, at least one layer is substantially made of the said propylene polymer or propylene polymer composition.

The said propylene polymer is a random copolymer (I) containing such an amount of comonomer(s) as to have a melting temperature (measured by DSC, i.e. Differential Scanning Calorimetry) of 155 °C or higher. When only ethylene is present as the comonomer, it is generally within 0.8 and 1.5% by weight with respect to the weight of the polymer. When C₄-C₁₀ α-olefins are present, they are generally within 1 and 4 wt% by weight with respect to the weight of the polymer.

Particularly preferred is a propylene polymer composition (II) comprising a first propylene (co)polymer (where the copolymer is a random copolymer) with an ethylene content between 0 and 1.5% by weight, and a second propylene random copolymer with an ethylene content between 0.8 and 5% by weight, the weight ratio of the second copolymer to the first (co)polymer being in the range from about 20:80 to about 80:20, preferably from 30:70 to 70:30, and the difference in the ethylene content between the two being preferably from 1 to 4 percentage units with respect to the weight of the (co)polymer concerned; or another propylene polymer composition (II) comprising a first propylene (co)polymer (where the copolymer is a random copolymer) with a comonomer content between 0 and 2% by weight, and a second propylene random copolymer with a comonomer content between 1.5 and 12% by weight, the weight ratio of the second copolymer to the first (co)polymer being in the range from about 20:80 to about 80:20, preferably from 30:70 to 70:30, and the difference in the comonomer content between the two being preferably from 1.5 to 10 percentage units with respect to the weight of the (co)polymer concerned, wherein the said comonomer is selected from C₄-C₁₀ α-olefins and mixtures thereof, with ethylene optionally being present.

The present invention also relates to the said propylene polymer compositions.

Preferably the Melt Flow Rate (MFR according to ISO 1133, 230 °C, 2.16 Kg load) of the said propylene polymer or polymer composition goes from 1 to 10 g/10 min., more preferably from 1 to 4 g/10 min..

Other preferred features for the compositions to be used for the films the present invention are:

Polydispersity Index (PI): from 3.5 to 7, more preferably from 3.8 to 5

The MFR values of the first propylene (co) polymer in composition (II) and of the second propylene random copolymer in composition (II) can be similar or substantially different.

In a particular embodiment of the present invention the MFR value of the first propylene (co) polymer is lower than that of the second propylene random copolymer and the difference in the MFR values being preferably greater than 5 g/10min...

The C₄-C₁₀ α-olefins, that may be present as comonomers in the said propylene polymer or polymer composition, are represented by the formula CH₂=CHR, wherein R is an alkyl radical, linear or branched, with 2-8 carbon atoms or an aryl (in particular phenyl) radical.

Examples of said C₄-C₁₀ α-olefins are 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene and 1-octene. Particularly preferred is 1-butene.

The compositions of the present invention can be prepared by polymerization in one or more polymerization steps. Such polymerization is carried out in the presence of stereospecific Ziegler-Natta catalysts. An essential component of said catalysts is a solid catalyst component comprising a titanium compound having at least one titanium-halogen bond, and an electron-donor compound, both supported on a magnesium halide in-active form. Another essential component (co-catalyst) is an organoaluminum compound, such as an aluminum alkyl compound.

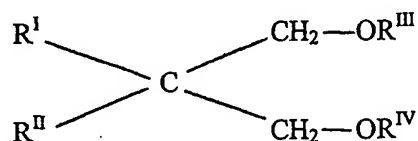
An external donor is optionally added.

The catalysts generally used in the process of the invention are capable of producing polypropylene with an Isotacticity Index greater than 90%, preferably greater than 95%.

Catalysts having the above mentioned characteristics are well known in the patent literature; particularly advantageous are the catalysts described in US patent 4,399,054 and European patent 45977. Other examples can be found in US patent 4,472,524.

The solid catalyst components used in said catalysts comprise, as electron-donors (internal donors), compounds selected from the group consisting of ethers, ketones, lactones, compounds containing N, P and/or S atoms, and esters of mono- and dicarboxylic acids.

Particularly suitable electron-donor compounds are 1,3-diethers of formula:



wherein R^I and R^{II} are the same or different and are C₁-C₁₈ alkyl, C₃-C₁₈ cycloalkyl or C₇-C₁₈ aryl radicals; R^{III} and R^{IV} are the same or different and are C₁-C₄ alkyl radicals; or are

the 1,3-diethers in which the carbon atom in position 2 belongs to a cyclic or polycyclic structure made up of 5, 6, or 7 carbon atoms, or of 5-n or 6-n' carbon atoms, and respectively n nitrogen atoms and n' heteroatoms selected from the group consisting of N, O, S and Si, where n is 1 or 2 and n' is 1, 2, or 3, said structure containing two or three unsaturations (cyclopolyenic structure), and optionally being condensed with other cyclic structures, or substituted with one or more substituents selected from the group consisting of linear or branched alkyl radicals; cycloalkyl, aryl, aralkyl, alkaryl radicals and halogens, or being condensed with other cyclic structures and substituted with one or more of the above mentioned substituents that can also be bonded to the condensed cyclic structures; one or more of the above mentioned alkyl, cycloalkyl, aryl, aralkyl, or alkaryl radicals and the condensed cyclic structures optionally containing one or more heteroatoms as substitutes for carbon or hydrogen atoms, or both.

Ethers of this type are described in published European patent applications 361493 and 728769.

Representative examples of said diethers are 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2-isopropyl-2-isoamyl-1,3-dimethoxypropane, 9,9-bis (methoxymethyl) fluorene.

Other suitable electron-donor compounds are phthalic acid esters, such as diisobutyl, dioctyl, diphenyl and benzylbutyl phthalate.

The preparation of the above mentioned catalyst components is carried out according to various methods.

For example, a $\text{MgCl}_2 \cdot n\text{ROH}$ adduct (in particular in the form of spheroidal particles) wherein n is generally from 1 to 3 and ROH is ethanol, butanol or isobutanol, is reacted with an excess of TiCl_4 containing the electron-donor compound. The reaction temperature is generally from 80 to 120 °C. The solid is then isolated and reacted once more with TiCl_4 , in the presence or absence of the electron-donor compound, after which it is separated and washed with aliquots of a hydrocarbon until all chlorine ions have disappeared.

In the solid catalyst component the titanium compound, expressed as Ti, is generally present in an amount from 0.5 to 10% by weight. The quantity of electron-donor compound which remains fixed on the solid catalyst component generally is 5 to 20% by moles with respect to the magnesium dihalide.

The titanium compounds which can be used for the preparation of the solid catalyst component are the halides and the halogen alcoholates of titanium. Titanium tetrachloride is the preferred compound.

The reactions described above result in the formation of a magnesium halide in active form. Other reactions are known in the literature, which cause the formation of magnesium halide in active form starting from magnesium compounds other than halides, such as magnesium carboxylates.

The active form of magnesium halide in the solid catalyst component can be recognized by the fact that in the X-ray spectrum of the catalyst component the maximum intensity reflection appearing in the spectrum of the nonactivated magnesium halide (having a surface area smaller than $3 \text{ m}^2/\text{g}$) is no longer present, but in its place there is a halo with the maximum intensity shifted with respect to the position of the maximum intensity reflection of the nonactivated magnesium dihalide, or by the fact that the maximum intensity reflection shows a width at half-peak at least 30% greater than the one of the maximum intensity reflection which appears in the spectrum of the nonactivated magnesium halide. The most active forms are those where the above mentioned halo appears in the X-ray spectrum of the solid catalyst component.

Among magnesium halides, the magnesium chloride is preferred. In the case of the most active forms of magnesium chloride, the X-ray spectrum of the solid catalyst component shows a halo instead of the reflection which in the spectrum of the nonactivated chloride appears at 2.56 \AA .

The Al-alkyl compounds used as co-catalysts comprise the Al-trialkyls, such as Al-triethyl, Al-triisobutyl, Al-tri-n-butyl, and linear or cyclic Al-alkyl compounds containing two or more Al atoms bonded to each other by way of O or N atoms, or SO_4 or SO_3 groups.

The Al-alkyl compound is generally used in such a quantity that the Al/Ti ratio be from 1 to 1000.

The electron-donor compounds that can be used as external donors include aromatic acid esters such as alkyl benzoates, and in particular silicon compounds containing at least one Si-OR bond, where R is a hydrocarbon radical.

Examples of silicon compounds are $(\text{tert-butyl})_2 \text{Si} (\text{OCH}_3)_2$, $(\text{cyclohexyl}) (\text{methyl}) \text{Si} (\text{OCH}_3)_2$, $(\text{phenyl})_2 \text{Si} (\text{OCH}_3)_2$ and $(\text{cyclopentyl})_2 \text{Si} (\text{OCH}_3)_2$. 1,3-diethers having the

formulae described above can, also be used advantageously. If the internal donor is one of these dieters, the external donors can be omitted.

In particular, even if many other combinations of the previously said catalyst components may allow to obtain polymers and polymer compositions having the previously said features 1) and 2), the random copolymers are preferably prepared by using catalysts containing a phthalate a inside donor and $(\text{cyclopentyl})_2 \text{Si} (\text{OCH}_3)_2$ as outside donor, or the said 1,3-diethers as inside donors.

As previously said, the polymerization process can be carried out in one or more steps. In the case of composition (II), it can be carried out in at least two sequential steps, wherein the first propylene (co)polymer and the second propylene random copolymer are prepared in separate subsequent steps, operating in each step, except the first step, in the presence of the polymer formed and the catalyst used in the preceding step. Clearly, when the composition (II) contains additional (co)polymers, it becomes necessary to add further polymerization steps to produce them. The said polymerization steps can be carried out in separate reactors, or in one or more reactors where gradients of monomer concentrations and polymerization conditions are generated. The catalyst is generally added only in the first step, however its activity is such that it is still active for all the subsequent step(s).

The regulation of the molecular weight is carried out by using known regulators, hydrogen in particular.

By properly dosing the concentration of the molecular weight regulator in the relevant steps, the previously described MFR values are obtained.

The whole polymerization process, which can be continuous or batch, is carried out following known techniques and operating in liquid phase, in the presence or not of inert diluent, or in gas phase, or by mixed liquid-gas techniques.

Reaction time, pressure and temperature relative to the two steps are not critical, however it is best if the temperature is from 20 to 100 °C. The pressure can be atmospheric or higher.

The catalysts can be pre-contacted with small amounts of olefins (prepolymerization).

It is also possible to employ a process for the catalytic polymerization in the gas-phase carried out in at least two interconnected polymerization zones, the process comprising feeding one or more monomers to said polymerization zones in the presence of catalyst under reaction conditions and collecting the polymer product from said polymerization zones, in which process the growing polymer particles flow upward through one of said

polymerization zones (riser) under fast fluidisation conditions, leave said riser and enter another polymerization zone (downcomer) through which they flow downward under the action of gravity, leave said downcomer and are reintroduced into the riser, thus establishing a circulation of polymer between the riser and the downcomer, the process being optionally characterised in that:

- means are provided which are capable of totally or partially preventing the gas mixture present in the riser from entering the downcomer, and
- a gas and/or liquid mixture having a composition different from the gas mixture present in the riser is introduced into the downcomer.

Such polymerization process is illustrated in WO 00/02929.

According to a particularly advantageous embodiment of this process, the introduction into the downcomer of the said gas and/or liquid mixture having a composition different from the gas mixture present in the riser is effective in preventing the latter mixture from entering the downcomer.

The composition (II) can also be obtained by preparing separately the said (co)polymers by operating with the same catalysts and substantially under the same polymerization conditions as previously explained (except that the said (co)polymers will be prepared in separate polymerization steps) and then mechanically blending said (co)polymers in the molten state. Conventional mixing apparatuses, like screw extruders, in particular twin screw extruders, can be used.

The propylene polymers and propylene polymer compositions used for the films of the present invention can also contain additives commonly employed in the art, such as antioxidants, light stabilizers, heat stabilizers, nucleating agents, colorants and fillers.

In particular, the addition of nucleating agents brings about a considerable improvement in important physical-mechanical properties, such as Flexural Modulus, Heat Distortion Temperature (HDT), tensile strength at yield and transparency.

Typical examples of nucleating agents are the p-tert.-butyl benzoate and the 1,3- and 2,4-dibenzylidenesorbitols.

The nucleating agents are preferably added in quantities ranging from 0.05 to 2% by weight, more preferably from 0.1 to 1% by weight with respect to the total weight.

The addition of inorganic fillers, such as talc, calcium carbonate and mineral fibers, also brings about an improvement to some mechanical properties, such as Flexural Modulus and HDT. Talc can also have a nucleating effect.

The application sector of the present invention is that of biaxially stretched films, frequently called BOPP (biaxially oriented polypropylene) films.

The films of the present invention can be prepared with the well known processes for the preparation of BOPPs, for example tentering or bubble blowing.

In the tentering process, the molten polymer materials are forced in continuous through a narrow slit. The extruded molten material is pulled away from the slit and cooled, then heated again and stretched both in the Machine Direction (MD), generally using heated rolls, and in the Transverse Direction (TD) with a tenter-frame.

In the bubble blowing process the molten polymer materials are forced through a circular shaped slip to form a tube. The film can be stretched contemporaneously in Machine and Transverse Direction.

In both processes the film can be finally subjected to an annealing (heat set) treatment.

The thickness of the films of the present invention is generally below 250 μm , preferably below 100 μm . They can be monolayer or multilayer films.

In the multilayer films, it is preferable that at least the base layer (also called "support layer") comprise the said propylene polymer or propylene polymer composition having the features 1) and 2). The other layer may comprise other kinds of polymers.

Examples of olefin polymers that can be used for the other layers are polymers or copolymers, and their mixtures, of $\text{CH}_2=\text{CHR}$ olefins where R is a hydrogen atom or a $\text{C}_1\text{-C}_8$ alkyl radical.

Particularly preferred are the following polymers:

- a) isotactic or mainly isotactic propylene homopolymers, and homopolymers or copolymers of ethylene, like HDPE, LDPE, LLDPE;
- b) crystalline copolymers of propylene with ethylene and/or $\text{C}_4\text{-C}_{10}$ α -olefins, such as for example 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, wherein the total comonomer content ranges from 0.05% to 20% by weight with respect to the weight of the copolymer, or mixtures of said copolymers with isotactic or mainly isotactic propylene homopolymers;

- c) elastomeric copolymers of ethylene with propylene and/or a C₄-C₁₀ α -olefin, optionally containing minor quantities (in particular, from 1% to 10% by weight) of a diene, such as butadiene, 1,4-hexadiene, 1,5-hexadiene, ethylidene-1-norbornene;
- d) heterophasic copolymers comprising a propylene homopolymer and/or one of the copolymers of item b), and an elastomeric fraction comprising one or more of the copolymers of item c), typically prepared according to known methods by mixing the components in the molten state, or by sequential polymerization, and generally containing the said elastomeric fraction in quantities from 5% to 80% by weight;
- e) 1-butene homopolymers or copolymers with ethylene and/or other α -olefins.

Examples of polymers different from polyolefins, employable for the other layers, are polystyrenes, polyvinylchlorides, polyamides, polyesters and polycarbonates.

Finally, the films of the present invention can undergo a series of subsequent operations, such as:

surface embossing, by heating the surface compressing it against the embossing roller;
printing, after having made the surface ink sensitive through oxidating (for instance flame) or ionizing treatments (for instance corona discharge treatment);
coupling with fabric or film, particularly polypropylene, by heating of the surfaces and compression;
coextrusion with other polymeric or metallic materials (e.g. aluminum film);
plating treatments (depositing a layer of aluminum through evaporation under vacuum, for example);
application of an adhesive layer on one of the two faces of the film, thus producing an adhesive film.

Depending upon the specific kind of film and final treatment, the films of the present invention can find many uses, the most important of which is goods and food packaging.

The following examples are given to illustrate the present invention without limiting purpose.

The data relating to the polymeric materials and the films of the examples are determined by way of the methods reported below.

- MFR: ISO 1133, 230 °C, 2.16 Kg;
- Melting temperature, melting enthalpy and solidification temperature: by DSC with a temperature variation of 20 °C per minute;

- ethylene content: by IR spectroscopy;
- Flexural Modulus: ISO 178;

Polydispersity Index (PI): measurement of molecular weight distribution of the polymer. To determine the PI value, the modulus separation at low modulus value, e.g. 500 Pa, is determined at a temperature of 200 °C by using a RMS-800 parallel plates rheometer model marketed by Rheometrics (USA), operating at an oscillation frequency which increases from 0.01 rad/second to 100 rad/second. From the modulus separation value, the PI can be derived using the following equation:

$$PI = 54.6 \times (\text{modulus separation})^{-1.76}$$

wherein the modulus separation (MS) is defined as:

$$MS = (\text{frequency at } G' = 500 \text{ Pa}) / (\text{frequency at } G'' = 500 \text{ Pa})$$

wherein G' is the storage modulus and G'' is the low modulus.

Fractions soluble and insoluble in xylene at 25 °C: 2.5 g of polymer are dissolved in 250 ml of xylene at 135 °C under agitation. After 20 minutes the solution is allowed to cool to 25 °C, still under agitation, and then allowed to settle for 30 minutes. The precipitate is filtered with filter paper, the solution evaporated in nitrogen flow, and the residue dried under vacuum at 80 °C until constant weight is reached. Thus one calculates the percent by weight of polymer soluble and insoluble at room temperature (25 °C).

TREF

About 1 g of sample is dissolved in 200 mL of o-xylene, stabilized with 0.1 g/L of Irganox 1010 (pentaerythrityl tetrakis 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate). The dissolution temperature is in the range of 125-135°C. The resulting solution is poured off into a column packed with glass beads and subsequently cooled down slowly in 16.5 h to 25°C.

The first fraction is obtained at room temperature eluting with o-xylene. The second fraction is collected after having raised the column temperature up to 95°C. The polymer component soluble between 25 and 95°C is collected as a single fraction.

The successive fractions are eluted with o-xylene while the temperature is raised linearly between 95 and 125°C. Each fraction, recovered as a 200 mL solution, is collected at 1°C temperature increments. The polymer fractions are subsequently precipitated with acetone, filtered on a 0.5 µm PTFE filter, dried under vacuum at 70°C, and weighted.

Examples 1 and 2 and Comp. Example 1

The polymers of Examples 1 and 2 are prepared by polymerizing propylene and ethylene under continuous conditions in a plant comprising a gas phase polymerisation apparatus.

The catalyst was sent to the gas phase polymerisation apparatus. The latter comprised two interconnected cylindrical reactors, riser 1 and downcomer 2. Fast fluidisation conditions were established in reactor 1 by recycling gas from the gas-solid separator.

The way to differentiate the gas composition in the two reactor legs was the "barrier" feed. This stream was propylene fed in the larger upper part of the downcomer.

The catalyst employed comprised a catalyst component prepared by analogy with Example 5 of EP A 728 769, but using microspheroidal $\text{MgCl}_2 \cdot 1.7 \text{ C}_2\text{H}_5\text{OH}$ instead of $\text{MgCl}_2 \cdot 2.1 \text{ C}_2\text{H}_5\text{OH}$.

Such catalyst component was used with dicyclopentyldimethoxysilane as external donor and with triethylaluminium (TEAL). The weight ratio TEAL/catalyst component was 5; the weight ratio TEAL/external donor was 4. Other operative conditions and the characteristics of the produced polymers are indicated in Table 1.

The main features of a conventional propylene polymer for BOPP are reported in Table 1 under Comp. 1.

Table 1

Ex.		1	2	Comp. 1
1 st component				
Temperature	°C	85	85	-
Split	wt%	≅ 50	≅ 50	-
C2-/(C2+C3-)	mol/mol	0.001	0.001	-
2 nd component				
Split	wt%	≅ 50	≅ 50	-
C2-/(C2+C3-)	mol/mol	0.01	0.01	-
MFR "L"	g/10 min.	1.5	1.5	1.8
C2- content	wt%	1.4	1.3	0
Xylene insoluble	wt%	97.3	98.1	95.5
Xylene soluble	wt%	2.7	1.9	4.5
Soluble fraction at the temperature: 25-95 °C	wt%	34.3	30.3	15.9
P.I.		4.42	4.43	4.8
Flexural Modulus	MPa	1500	1500	1600
D.S.C. Melting temperature	°C	158.7	158.6	165.1
D.S.C. Melting enthalpy	J/g	96.7	95.3	94.8
D.S.C. Solidific. Temperature	°C	106.6	107.4	112.6
Cast film 50 micron				
Haze	%	8.5	8.4	-
Gloss 60°	%	58.5	59	-
Fish eyes >0.2 mm	n°/m ²	230	190	200
Fish eyes 0.5-0.7 mm	n°/m ²	4	4	2
Fish eyes 0.7-1.5 mm	n°/m ²	1	0	0
Fish eyes >1.5 mm	n°/m ²	0	0	0

Note:

1st component = polymer produced in downcomer;

2nd component = polymer produced in riser;

Split = amount of polymer produced;

wt% = % by weight;

C2- = ethylene;

C3- = propylene;

$C2-/(C2-+C3-)$ = monomer feed ratio.

The polymers of the examples were biaxially stretched at different temperatures on a laboratory TM long stretcher. Figure 1 reports the biaxial stress at yield measured at the TM-long film stretcher as a function of the stretching temperature. With respect to Comp. 1, the polymers of Ex. 1 and 2 showed substantially lower values of the biaxial stress at yield and a lower minimum stretching temperature.

Ex. 3 to 5 and Comp. 2

The polymers of Examples 1 and 2 are prepared under the same conditions as in Ex. 1 and 2.

Other operative conditions and the characteristics of the produced polymers are indicated in Tables 2 and 3.

The main features of a conventional propylene polymer for BOPP are reported in Tables 2 and 3 under Comp. 2.

Table 2

Example		3	4	5	Comp. 2
1 st component					
Temperature	°C	85	88	88	-
Split	wt%	≅ 50	≅ 50	≅ 50	-
C2-/(C2-+C3-)	mol/mol	0.001	< 0.001	< 0.001	-
2 nd component					
Split	wt% :	≅ 50	≅ 50	≅ 50	-
C2-/(C2-+C3-)	mol/mol	0.013	0.015	0.01	-
MFR "L"	g/10 min.	1.7	2.0	1.7	1.8
C2- content	wt%	1.1	1.6	1.2	≅0.6
Xylene insoluble	wt%	98.2	97.4	98.1	94.5
Xylene soluble	wt%	1.8	2.6	1.9	5
I.V.	dl/g	2.58	2.45	2.37	-
P.I.		4.75	4.55	4.75	4.6
Flexural Modulus	MPa	1475	1255	1535	1385
D.S.C. Melting Temperature	°C	159.2	157.5	160.2	161.7
D.S.C. Melting enthalpy	J/g	99.9	94.3	101.8	91.6
D.S.C. Solidific. Temperature	°C	109.8	104.3	107.8	107.1

Table 3

Polymer of Ex.	I.V.	Soluble fraction at the temperature:		T _p
		25-95 °C	95-115 °C	
	(dl/g)	(wt%)	(wt%)	(°C)
3	2.58	22.6	76.1	107
4	2.45	50.9	48.0	105
5	2.37	27.2	71.1	106
Comp. 2	-	27.6	67.6	107

A-B-A structured BOPP film samples with a thickness of 20 μ m were made with the polymers of these examples. The skin layers consisted of the same resin as the core. The machine direction stretching ratio was 5 * 1.1 and the transverse direction stretch ratio was between 8.3 and 8.5.

In order to define the processability of the various grades a process evaluation was carried out. For each resin the thickness profile, stretchability and the amount of breakages during processing were determined.

The properties of the films are shown in Table 4.

Table 4

Polymer of Ex.	MIN. PHT (°C)	Thickness Profile (Standard Deviation)	Young Modulus (MPa)		WVTR (g/m ² /day)	OTR (cc/m ² /day)	Haze
			MD	TD			
3	150.5	0.028	5250 \pm 15	2390 \pm 20	4.9	1620	0.93 \pm 0.08
4	145	0.036	5040 \pm 35	2250 \pm 30	5.0	1970	0.64 \pm 0.08
5	139.5	0.030	4260 \pm 55	2050 \pm 20	6.2	2260	0.59 \pm 0.07
Comp. 2	145	0.048	4760 \pm 50	2150 \pm 40	5.5	2210	0.67 \pm 0.05

The min. PHT (pre heating temperature) in TD is a key parameter used to specify the processability. The minimum PHT is the lowest stretching temperature in the TD preheating zone which can be reached before breakage without having stretching bands. There is a general perception in BOPP that a grade which can be processed at low PHT's has a better processability. BOPP producers even indicate that such grades would generally have a better performance on high speed BOPP lines.

The thickness profile was checked by monitoring the thickness variation of the film (2 σ) in function of the time. The thickness variation was recorded for all the examples during a period of approximately 30 minutes. Looking at the data reported it is clear that all the polymers representing the invention had a more uniform thickness profile compared to that of the reference material (Comp. 2).

No breakages were observed for all the materials submitted to this study.

The film characterisation includes the determination of the optical, mechanical and barrier properties.

The mechanical properties of the film were measured in MD and TD. The work was done on an Instron according to ASTM 882. The Oxygen (OTR) and the Water Vapour Transmission Rate (WVTR) were determined on all resins submitted to this study. The OTR was measured at an ambient temperature of 23°C with a humidity degree of 60-70%. The WVTR is determined at the same test conditions but with a relative humidity of 90%.

The polymer of Ex. 4 showed the best overall processability performance and had mechanical and barrier properties almost aligned with those of Comp. 2.

The polymers of Ex. 3 and 5 had processing temperatures similar to those of Comp. 2, with better mechanical and barrier properties. The polymers of Ex. 2 to 4 showed in comparison with Comp. 2 a more uniform thickness profile.

Ex. 6 and Comp. 3

The polymer of Ex. 6 is prepared under the same conditions as in Ex. 1 and 2.

Other operative conditions and the characteristics of the produced polymers are indicated in Table 5.

The main features of a conventional propylene polymer for BOPP are reported in Table 5 under Comp. 3.

Table 5

Ex.		6	Comp. 3
1 st component			
Temperature	°C	85	-
Split	wt%	≅ 50	-
C2-/(C2-+C3-)	mol/mol	0.001	-
2 nd component			
Split	wt%	≅ 50	-
C2-/(C2-+C3-)	mol/mol	0.01	-
MFR "L"	g/10 min.	1.5	3.5
C2- content	wt%	1.4	0
Xylene insoluble	wt%	97.3	95.5
Xylene soluble	wt%	2.7	4.5
Soluble fraction at the temperature: 25-95 °C	wt%	34.3	21
P.I.		4.42	5.5
Flexural Modulus	MPa	1500	1490
D.S.C. Melting temperature	°C	158.7	160.4
D.S.C. Melting enthalpy	J/g	96.7	95.2
D.S.C. Solidific. Temperature	°C	106.6	107.7
Cast film 50 micron			
Haze	%	8.5	16.7
Gloss 60°	%	58.5	34.4
Fish eyes >0.2 mm	n°/m ²	230	200
Fish eyes 0.5-0.7 mm	n°/m ²	4	2
Fish eyes 0.7-1.5 mm	n°/m ²	1	0
Fish eyes >1.5 mm	n°/m ²	0	0

A trial similar to that reported in Ex. 1 was carried out at a BOPP pilot line. With respect to Comp. 3, the polymer of Ex. 6 showed a slightly lower minimum pre-heating temperature and improved mechanical and optical properties. With respect to Comp. 1, the polymer of Ex. 6 showed similar mechanical properties and a substantially lower minimum pre-heating temperature.

Thus, the polymers used of the films of the invention, compared to conventional polymers of substantially the same MFR, provide a substantially improved balance of elevated temperature drawing behaviour and mechanical properties of oriented film made therefrom.

The results are reported in Table 6 wherein also the properties of a film obtained by processing, under the same conditions, the polymer of Comp. 1 are reported.

Table 6

Polymer of Ex.	MIN. PHT (°C)	Young Modulus (MPa)		Haze
		MD	TD	
6	150	2036	3566	1.03
Comp. 1	154	2026	3617	-
Comp. 3	152	2022	3392	1.36

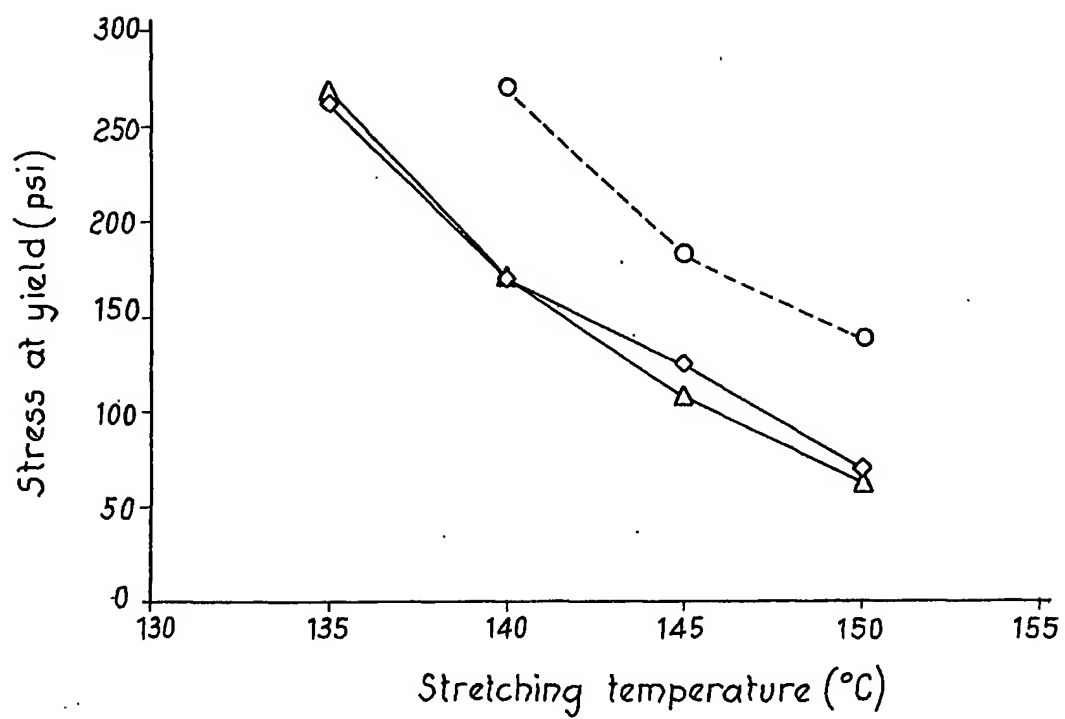
CLAIMS

1. Bioriented polypropylene film (BOPP) wherein at least one layer comprises a propylene polymer containing at least 0.8% by weight of ethylene and optionally one or more C₄-C₁₀ α -olefins, or a propylene polymer composition containing at least 0.8% by weight of one or more comonomers selected from ethylene and C₄-C₁₀ α -olefins, said polymer or polymer composition having the following features:
 - 1) a melting temperature of 155 °C or higher;
 - 2) a content of fraction soluble in xylene at room temperature (about 25 °C) lower than 3% by weight, and a value of the ratio of the polymer fraction collected in the temperature range from 25°C to 95°C to the fraction soluble in xylene at room temperature higher than 8 wt%/wt%.
2. The BOPP of claim 1, wherein the Melt Flow Rate (MFR according to ISO 1133, 230 °C, 2.16 Kg load) of the said propylene polymer or polymer composition is from 1 to 10 g/10 min.
3. The BOPP of claim 1, wherein at least one layer comprises a propylene random copolymer (I) in which, when only ethylene is present as the comonomer, it is within 0.8 and 1.5% by weight with respect to the weight of the polymer, when C₄-C₁₀ α -olefins are present, they are generally within 1 and 4 wt% by weight with respect to the weight of the polymer.
4. The BOPP of claim 1, wherein at least one layer comprises a propylene polymer composition (II) comprising a first propylene (co)polymer (where the copolymer is a random copolymer) with an ethylene content between 0 and 1.5% by weight, and a second propylene random copolymer with an ethylene content between 0.8 and 5% by weight, the weight ratio of the second copolymer to the first (co)polymer being in the range from about 20:80 to about 80:20, and the difference in the ethylene content between the two being preferably from 1 to 4 percentage units with respect to the weight of the (co)polymer concerned.
5. The BOPP of claim 1, wherein at least one layer comprises a propylene polymer composition (II) comprising a first propylene (co)polymer (where the copolymer is a random copolymer) with a comonomer content between 0 and 2% by weight, and a second propylene random copolymer with a comonomer content between 1.5 and 12% by weight, the weight ratio of the second copolymer to the first (co)polymer

being in the range from about 20:80 to about 80:20, and the difference in the comonomer content between the two being preferably from 1.5 to 10 percentage units with respect to the weight of the (co)polymer concerned, wherein the said comonomer is selected from C₄-C₁₀ α -olefins and mixtures thereof, with ethylene optionally being present.

6. A propylene polymer composition comprising a first propylene (co)polymer (where the copolymer is a random copolymer) with an ethylene content between 0 and 1.5% by weight, and a second propylene random copolymer with an ethylene content between 0.8 and 5% by weight, the weight ratio of the second copolymer to the first (co)polymer being in the range from about 20:80 to about 80:20, and the difference in the ethylene content between the two being preferably from 1 to 4 percentage units with respect to the weight of the (co)polymer concerned, said composition having the following features:
 - 1) a melting temperature of 155 °C or higher;
 - 2) a content of fraction soluble in xylene at room temperature (about 25 °C) lower than 3% by weight, and a value of the ratio of the polymer fraction collected in the temperature range from 25°C to 95°C to the fraction soluble in xylene at room temperature higher than 8 wt%/wt%.
7. A propylene polymer composition comprising a first propylene (co)polymer (where the copolymer is a random copolymer) with a comonomer content between 0 and 2% by weight, and a second propylene random copolymer with a comonomer content between 1.5 and 12% by weight, the weight ratio of the second copolymer to the first (co)polymer being in the range from about 20:80 to about 80:20, and the difference in the comonomer content between the two being preferably from 1.5 to 10 percentage units with respect to the weight of the (co)polymer concerned, wherein the said comonomer is selected from C₄-C₁₀ α -olefins and mixtures thereof, with ethylene optionally being present, said composition having the following features:
 - 1) a melting temperature of 155 °C or higher;
 - 2) a content of fraction soluble in xylene at room temperature (about 25 °C) lower than 3% by weight, and a value of the ratio of the polymer fraction collected in the temperature range from 25°C to 95°C to the fraction soluble in xylene at room temperature higher than 8 wt%/wt%.

1/1

Fig.1

○ = Comp.1

△ = Ex.1

◇ = Ex.2